PB81-100307

Distribution and Movement of Toxaphene in Anaerobic Saline Marsh Soils

(U.S.) Corvallis Environmental Research Lab., OR

1 Jan 78

U.S. Department of Commerce
National Technical Information Service
NTIS.

ERL-Cor-043J

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before complete

1. REPORT NO.	2.	3.
EPA-600/J-79-102	JOURNAL ARTICLE	PB81-100307

4. TITLE AND SUBTITLE	5. REPORT DATE
Distribution and Movement of Toxaphene in Anaerobic Saline Marsh Soils	1979
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
John L. Gallagher, Sarah E. Robinson, W. J. Pfeiffer and Denise M. Seliskar	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Research Laboratory-Corvallis Office of Research and Development U.S. Environmental Protection Agency Corvallis, Oregon 97330	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
SAME	Journal
	14. SPONSORING AGENCY CODE
	600/02

15. SUPPLEMENTARY NOTES

Published in Hydrobiologia Vol. 63, 1, p. 3-9, 1979

16. ABSTRACT

The distribution and method of movement of a hydrophobic pesticide through anaerobic saline marsh soils profiles was investigated. In the study are the flooding tidal water contained low concentrations of toxaphene. The compound accumulated only slightly in the marsh soils not flooded daily by the tides. Pesticide concentrations in the marsh soils generally decreased with depth. Dissection of the soil horizons revealed many micro-habitats with differing toxaphene concentrations. In all of the soil profiles the toxaphene concentration was greater in the macro-organic matter (MOM) than in the MOM-free soil. Highest pesticide concentrations were associated with the dead roots.

Toxaphene added below the soil surface was absorbed into the plant tissue from both sandy and silty clay loam marshes. Birectional translocation occurred, with toxaphene moving down to the roots, as well as upward into the stems. The highest concentrations were in the underground plant parts. Translocation in Spartina alterniflora roots represents a rapid method of moving toxaphene through these waterlogged anaerobic soils.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to Public	Unclassified	
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA-600/J-79-102
JOURNAL ARTICLE

Hydrobiologia vol. 63, 1, pag. 3-9, 1979

DISTRIBUTION AND MOVEMENT OF TOXAPHENE IN ANAEROBIC SALINE MARSH SOILS[1]

John L. GALLAGHER[3], Sarah E. ROBINSON, William J. PFEIFFER & Denise M. SELISKAR[2]

[1] Supported by grants from Hercules, Inc. and the Sapelo Island Research Foundation, Inc. Contribution No. 348 from the University of Georgia Marine Institute, Sapelo Island, Georgia 31327.
[2] Associate Marine Scientist, Research Technician I, Research Technician II, and Research Technician II, the University of Georgia Marine Institute, Sapelo Island, Georgia 31327.

[3] Present address: Environmental Protection Agency, Corvallis Environmental Research Laboratory, 200 SW 35th St., Corvallis, Oregon 97330

Received January 1, 1978

Keywords: pesticides. *Spartina*. translocation. leaching.

Abstract

The distribution and method of movement of a hydrophobic pesticide through anaerobic saline marsh soil profiles was investigated. In the study area the flooding tidal water contained low concentrations of toxaphene. The compound accumulated only slightly in the marsh soils not flooded daily by the tides. Pesticide concentrations in the marsh soils generally decreased with depth. Dissection of the soil horizons revealed many micro-habitats with differing toxaphene concentrations. In all of the soil profiles the toxaphene concentration was greater in the macro-organic matter (MOM) than in the MOM-free soil. Highest pesticide concentrations were associated with the dead roots.

Toxaphene added below the soil surface was absorbed into the plant tissue from both sandy and silty clay loam marshes. Bi-rectional translocation occurred, with toxaphene moving down to the roots, as well as upward into the stems. The highest concentrations were in the underground plant parts. Translocation in *Spartina alterniflora* roots represents a rapid method of moving toxaphene through these waterlogged anaerobic soils.

Introduction

Toxaphene is relatively insoluble in aqueous solution and consequently it has been concluded that it is not leached through soil profiles (Taschenberg *et al.*, 1961). Studies on a Vertisol (Houston black clay) in Texas indicated 90 to 95% of the toxaphene was found in the upper 12 inches (Swoboda *et al.*, 1971). In a Dunbar soil in South Carolina, the bulk of the surface-applied toxaphene remained in the A horizon although some moved to the horizon below 81 cm and small quantities were present in the ground water (La Fleur *et al.*, 1973). The anaerobic saline soils in a marsh ecosystem near Brunswick, Georgia, have been exposed to toxaphene contaminated industrial waste water for more than 20 years. Recent pollution abatement procedures have reduced the apparent concentration of toxaphene in the manufacturing plant effluent from 2000 ppb in 1970 to less than 7 ppb in 1974 (Reimold, unpub. ms.). Recently Durant & Reimold (1972) reported toxaphene concentrations in sediment cores from an estuary near Brunswick, Georgia, which has been receiving industrial waste water containing toxaphene. They also reported finding the pesticide in *Spartina alterniflora* Loisel. growing in the marshes bordering the creeks (Reimold & Durant, 1974). These results raised questions about the partitioning of toxaphene between the several compartments (living plant tissue, dead plant tissue, rhizosphere soil, non-rhizosphere soil) within a given horizon as well as between soil horizons from various soil profiles in the marsh. Is the toxaphene generally distributed within a horizon or are there micro-habitats having greater or lesser concentration?

Since toxaphene is only slightly soluble in aqueous solution and water moves very slowly through salt marsh

Dr. W. Junk b.v. Publishers - The Hague, The Netherlands

soils (Gallagher & Daiber, 1974), we also questioned if the plants might play a role in carrying toxaphene down into the soil profile.

Materials and methods

In June 1974 cores were collected from the marsh bordering Dupree Creek near Brunswick, Georgia, approximately 0.1 km from the manufacturing plant discharge ditch. Triplicate cores were taken from the high elevation *Spartina alterniflora* marsh, between plant stems on the creekbank, over stems on the creekbank and in the nonvegetated creekbank between the grass and the permanently flooded portion of the creek, using an aluminum device (Gallagher, 1974). The creekbank and nonvegetated areas are inundated by the tides (average amplitude approximately 2 m) twice during most days while tidal water reaches the high marsh less than half of the days. Aerial portions of the plants associated with the areas cored, as well as the cores, were returned to the laboratory where the cores were sectioned into naturally occurring soil horizons.

In August a second series of cores was taken at the junction of Terry Creek and Dupree Creek about 0.4 km from the waste water ditch. Cores were stored on ice until they were processed the next day. Three cores were sectioned and the whole segment extracted while a like number were separated into macro-organic matter (MOM) (that not passing a 1 mm sieve) and the MOM-free soil (MUD) fractions before processing and analysis. A third set of triplicate marsh cores collected in December was dissected in more detail in the laboratory. The plants were pulled gently from the soil and the aerial and underground portions separated for analysis. The underground portion consisting of roots and rhizomes with adhering soil was further subdivided by washing the soil from the roots and collecting the muddy water which was evaporated to dryness at room temperature. The soil collected from washing the roots was considered to be the rhizosphere soil. The portion of the soil core remaining after the removal of the living plant was divided into dead roots and dead matter (rhizomes, stem bases, unknowns), both with adhering mud. Each of these categories was subdivided into MOM and MUD by washing.

In September 1974, 12.5 cm diameter plexiglass tubing was used to remove three 35 cm deep cores from a *S. alterniflora* marsh developed on sandy soil behind a barrier bar on the eastern side of Sapelo Island, Georgia. A fourth core was taken in a silty clay loam marsh in the Duplin River marsh on the western side of Sapelo Island. All cores were taken in such a way as to include a number of established plants. The outside of each core was covered with aluminium foil to prevent light from stimulating algal growth at the plastic-soil interface. The cores were placed in the greenhouse for several weeks of acclimatization.

On 8 October enough commercial grade (72%) toxaphene (formulated with aliphatic petroleum derivatives by Kerr McGee Chemical Corp. using toxaphene manufactured by Hercules, Inc.) was injected with a syringe and needle at a depth of 1 cm to produce 3 ppm in the soil if it were distributed uniformly. The cores were returned to the greenhouse where they were watered daily with tap water (50 mls in the sand cores and 25 mls in the mud). This water program kept the soils saturated most of the time. After each watering a few mls of water accumulated in the dish in which the sand cores sat. After 2 weeks the cores were returned to the lab and dissected by cutting each into sections of 0-1.5 cm, 10-20 cm, and 20 cm to base of the core. The samples from the sand marsh were air dried and then the macro-organic matter (MOM) separated from the sand by sieving followed by drying. Prior to drying the aerial portion of the plants was separated into inflorescences, leaves, and stems. The plant tissue was ground with a Wiley Mill with a 40 mesh screen prior to analysis.

Analytical procedures were similar to those by Durant and Reimold (1972). Following Soxhlet extraction with petroleum ether, concentration and partitioning with acetonitrile, the residue was evaporated nearly to dryness on a steam table. The residue was taken up in petroleum ether and eluted from a Florisil column with 6% ethyl ether in petroleum ether. The extracts were analyzed by electron capture gas chromatography and the concentration calculated by comparing five peak heights from the sample with those from a standard injected before each sample.

Results and discussion

Concentration profiles of toxaphene in the soil show only small quantities of the pesticide accumulate in the high marsh above the elevation which is flooded daily by the tides (Fig. 1, 2). Although the same patterns of toxaphene distribution were seen at the Dupree Creek and Terry Creek sites, the toxaphene concentrations were lower

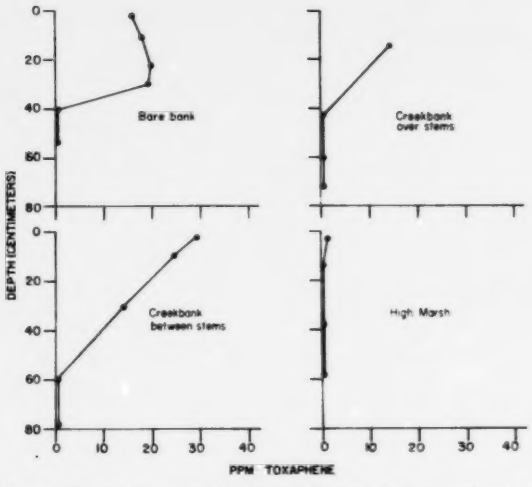

Fig. 1. Toxaphene concentration profiles of whole cores from a *Spartina alterniflora* salt marsh along Dupree Creek (June 1974).

(Fig. 2) at the latter site. The difference between the sites may be attributed to either seasonal differences due to sampling date (June vs. August) or to lower input as the result of the Terry Creek site being further from the manufacturing plant outfall. When we compared the set of Dupree Creek cores taken in June with a set collected in January the difference was less than 30%. The comparison of the creekbank surface soils between Dupree and Terry Creek showed the difference to be 95% less at the more distant station. Thus it seems that the distance from the outfall rather than the season of collection was the major reason for the difference.

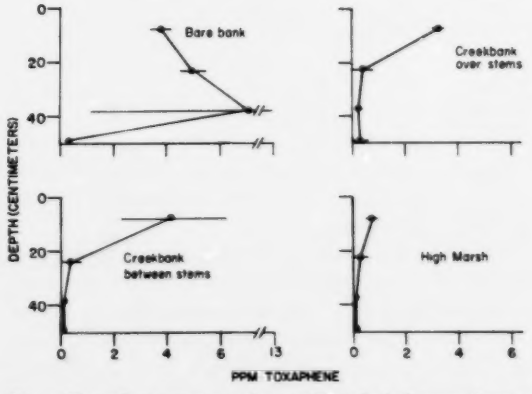

Fig. 2. Toxaphene concentration profiles of whole cores from a *Spartina alterniflora* salt marsh along Terry Creek (August 1974).

Within the 18-28 cm horizon in the creekbank on Dupree Creek, a third of the mass was composed of light-colored mottles within the dark matrix. Toxaphene concentration was 27.9 ppm in the dark zones which were rich in micro-organic matter (that passing a 1 mm sieve), and only 4.0 ppm in the light-colored soil. Since the greater concentration was associated with the organic-rich fraction, we compared the MOM with the MUD.

In the upper 45 cm of soil in the high marsh in August at the Terry Creek site the toxaphene was approximately 5 times more concentrated in the MOM (Fig. 3) than in the MUD (Fig. 4). In the creekbank area the MOM contained more than 10 times the concentration of the toxaphene found in the MUD. Although the concentrations of toxaphene in MOM are much higher than in MUD, the relatively low quantity of MOM compared with MUD resulted in more of the toxaphene in the soil profile being in the MUD in the high marsh and the bare bank (Table 1). In the vegetated creekbank areas somewhat more of the toxaphene was in the MOM than the MUD. Agreement between the whole core and the sum of the partitioned cores was poor in these two areas. We attribute this to the greater variability of MOM distribution in creekbank cores than those from high marsh (Gallagher, 1974).

Since the simple dissections into MOM and MUD revealed striking differences we decided to extend this approach and separate the soil into more components. These analyses produced a wide range of concentrations (Table 2). The rhizosphere soil of the live roots and that associated with the dead matter were nearly identical in toxaphene concentration. The similarity of these fractions could be simply interpreted to suggest there was little exchange between the MOM and the adjacent soil

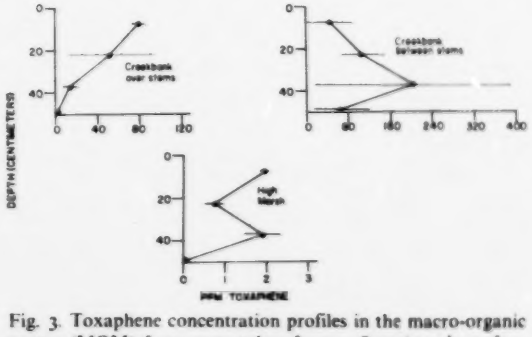

Fig. 3. Toxaphene concentration profiles in the macro-organic matter (MOM) from cores taken from a *Spartina alterniflora* salt marsh along Terry Creek (August 1974).

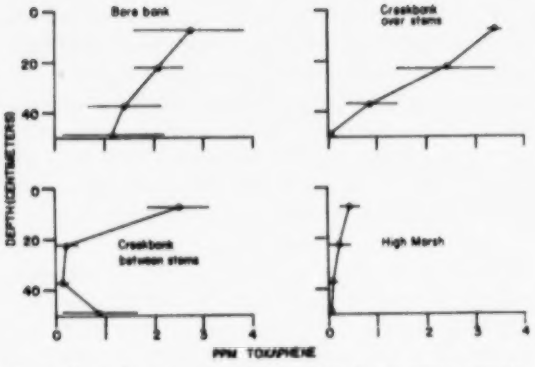

Fig. 4. Toxaphene concentration profiles in the macro-organic matter free soil (MUD) from a *Spartina alterniflora* salt marsh along Terry Creek (August 1974).

zones. This view is supported by our earlier observation that in the dark organic matter-rich soil zone the toxaphene was more abundant. No MOM was present, only micro-organic matter, yet there was still a large concentration gradient across the dark-light interface.

Examination of whole core segments rather than these microhabitats within the soil could give a misleading picture of the toxaphene concentrations to which various populations of organisms are exposed. Organisms utilizing the MOM in the soil for food or habitation may be exposed to concentrations at least fify times greater than that in the overall soil system. Conversely, organisms associated with the MUD would be exposed to

Table 1. Toxaphene in whole core segments, macro-organic matter (MOM) and remaining soil (MUD) from cores of a *Spartina alterniflora* marsh near the junction of Terry and Dupree creeeks near Brunswick, Ga. (mg m^{-2}).

	Depth (cm)	Whole cores mg m^{-2}	Partitioned core MOM mg m^{-2}	Partitioned core MUD mg m^{-2}
high marsh	0-15	27.5 ± 6.9	7.9 ± 2.1	15.0 ± 3.1
	15-30	11.2 ± 13.2	3.7 ± 1.4	5.4 ± 1.4
	30-45	0	1.2 ± 0.2	2.8 ± 2.6
	45-55	0	0	
	Total	40.7 ± 4.7	12.8 ± 3.5	23.2 ± 4.1
creekbank (between stems)	0-15	190.2 ± 40.5	127.6 ± 106.3	102.5 ± 15.2
	15-30	10.1 ± 10.1	104.1 ± 36.8	30.2 ± 10.2
	30-45	0	100.0 ± 47.5	5.8 ± 5.8
	45-55	0	54.6 ± 47.9	37.0 ± 30.2
	Total	132.8 ± 30.6	406.7 ± 61.1	155.5 ± 35.6
creekbank (over stems)	0-15	163.9 ± 3.9	168.8 ± 75.4	125.6 ± 11.5
	15-30	23.6 ± 23.6	172.5 ± 109.7	90.5 ± 15.6
	30-45	10.7 ± 10.2	18.1 ± 1.0	36.1 ± 19.6
	45-55	12.8 ± 12.8	1.8 ± 1.6	0
	Total	206.1 ± 57.3	361.2 ± 183.5	252.2 50.8
bare bank	0-15	60.1 ± 8.1		37.6 ± 16.9
	15-30	61.0 ± 5.0		47.5 ± 17.6
	30-45	176.4 ± 67.5		36.7 ± 20.1
	45-55	7.6 ± 2.4		23.6 ± 20.7
	Total	305.6 ± 109.0	10.6 ± 1.2	104.7 ± 14.1

•because of small quantity of MOM, all samples for a core were pooled.

Table 2. Toxaphene concentration in various parts of a dissected *Spartina alterniflora* salt marsh.

	Toxaphene concentration (ppm)
shoots	6.3 ± 0.9
live roots and rhizomes	1.6 ± 0.4
rhizosphere soil	0.9 ± 0.04
dead roots	93.9 ± 32.1
soil from near dead roots	0.9 ± 0.2
dead matter*	16.9 ± 5.2
soil from near dead matter	1.4 ± 0.8

* Includes rhizomes, stem bases and unknowns.

concentrations much lower than the average.

Unless toxaphene degradation processes in the salt marsh environment follow zero order kinetics, the different concentrations in the various microhabitats are important in determining rates.

When the concentrations in the various components of the MOM fraction were examined, the lower toxaphene concentration in the living parts was striking. It may be that the loss of cell surface integrity and the development of numerous minute cracks and fissures in the cell surfaces, and the added surface due to the microbial populations and the sediments trapped in the dead material

provide sites for adsorption and absorption of toxaphene as it percolates slowly through the soil. The large surface area with a high potential for adsorption and absorption is shown for leaf tissue in Fig. 5. Alternatively, or additionally, the toxaphene might have been absorbed by the living roots and concentrated as the natural organic compounds were broken down by microbes during root senescence and subsequent decay. If toxaphene was degraded more slowly than the natural root components, it would become more concentrated as decay progressed.

Reimold & Durant (1974) have reported significant quantities of toxaphene in *Spartina alterniflora* shoots from a toxaphene contaminated marsh. Those plants could have removed the toxaphene from either the soil or the tidal water immersing the leaves.

In order to follow the distribution of toxaphene from the soil into the plants and within the soil we spiked cores of uncontaminated marsh. After an incubation period aerial parts of the plant were harvested, the soil and MOM were separated and the fractions analyzed. The results of the analyses of the MOM and the remainder of the soil in both the sand and silty clay loam (MUD) cores used in the toxaphene movement experiments are shown in Fig. 6. In both the sand and silty clay loam cores, toxaphene displayed a higher affinity for MOM than the remainder of the soil. In both cases only trace concentrations of toxaphene were found below 10 cm indicating movement by leaching through the soil was slight. The apparent slight rise in concentration in MOM in the deepest layer in the sand marsh may be because of accumulation at the broken ends of roots which extended beyond the depth of coring in the marsh. There was little apparent movement upward in the sand, whereas in the silty clay loam the concentration was highest at the sur-

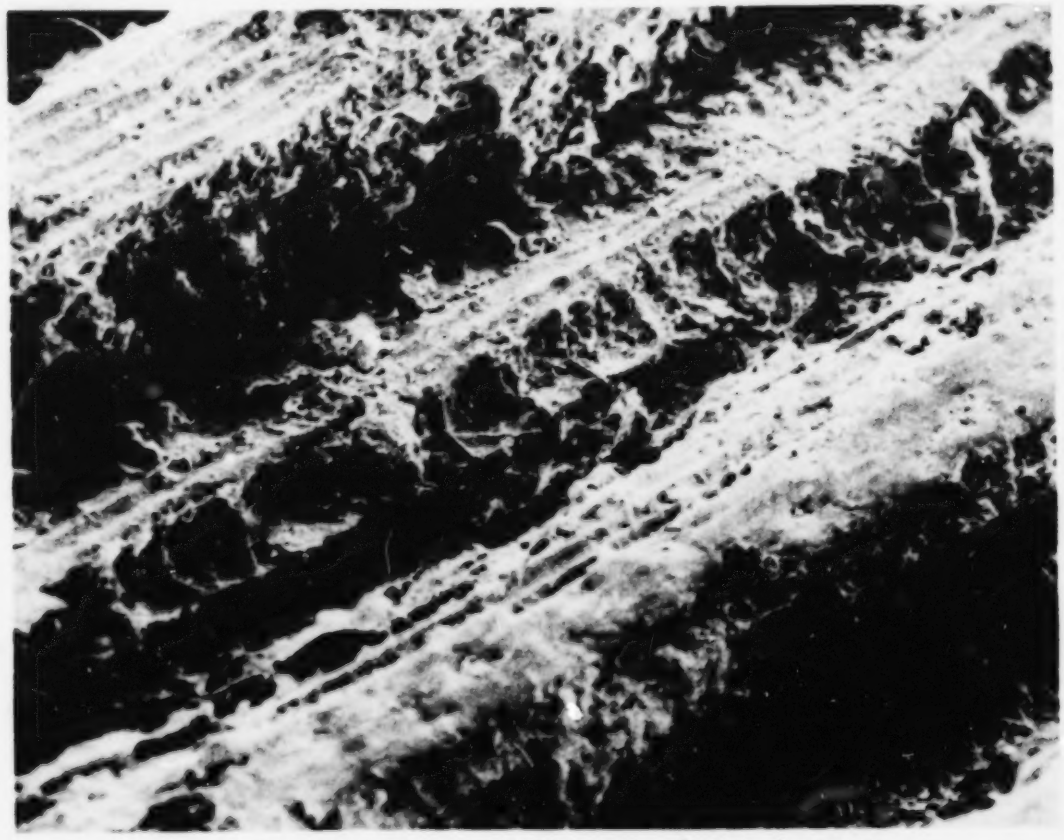

Fig. 5. Scanning election micrograph of a dead *Spartina alterniflora* leaf surface. (500 x).

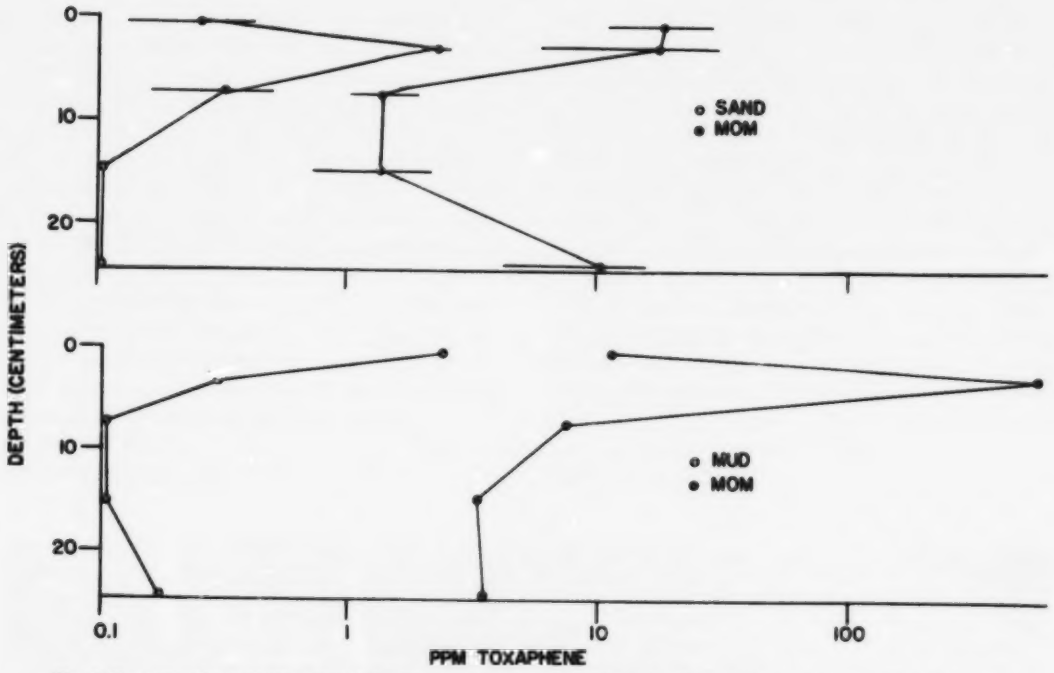

Fig. 6. Concentrations of toxaphene in macro-organic matter (MOM) and soil (mud or sand) from cores of *Spartina alterniflora* marsh injected with pesticide at the 2.5 cm. depth.

face. Perhaps the upward movement of solution in the soil capillaries during surface evaporation is more effective in the finer textured soil.

Although concentrations were generally higher in the MOM near the surface there were significant quantities at the bottom of the cores. It is possible that it moved to the lower horizons through the sand and mud and only then was absorbed by the plant material. It is more likely that it was translocated to that depth within the root system since the stems, leaves, and inflorescences also contained toxaphene (0.3, 1.3, 1.5 ppm respectively) indicating these plants absorbed the pesticide from the soil and actually translocated it in the living tissue both acropetally and basipetally.

When the amount rather than the concentration of toxaphene is considered, the distribution picture appears somewhat different (Table 3). In the sandy marsh where the underground biomass was relatively low, most of the toxaphene remained in the soil at about the same depth as it was applied. Most of the pesticide also stayed at the application depth in the finer textured soil marsh core but most was bound to the more abundant MOM. Be-

Table 3. Distribution (per cent) of toxaphene in various components of the *Spartina alterniflora* soil complex.

	Aerial	Underground (Depth in cm)				
		0-1.5	1.5-5.0	5.0-10.0	10.0-20.0	20.0-base
Sandy marsh						
inflorescences	0.3					
leaves	0.6					
stems	0.1					
MOM		2.2	3.7	1.3	0.4	0.3
sand		2.4	63.2	14.3	5.7	6.7
Silty clay loam marsh						
inflorescences	0.1					
leaves	0.2					
stems	0.1					
MOM		4.2	60.4	6.4	0.3	0.4
MUD		13.4	5.1	8.0	4.8	13.2

cause of the large mass of sand and mud compared to the quantity of MOM, the total amount in that phase below the injection point was great even though the concentration was very low.

Four points can be made from these studies on the distribution and movement of toxaphene in saline marsh soils. First, the accumulation in the soil is significant only where the substrates are frequently subjected to tidal flooding by contaminated water. Second, the concentration decreases with depth. Third, organisms living in different microhabitats are subjected to toxaphene concentrations which may have a 50-fold range. Fourth, the toxaphene distribution patterns seen in the marsh soils in contaminated estuaries are the function of basipetal and acropetal plant translocation, as well as leaching, degradation and the pesticide concentration at the time of substrate deposition.

References

Durant, C. J. & Reimold, R. J. 1972. Effects of estuarine dredging of toxaphene-contaminated sediments in Terry Creek, Brunswick, Ga. - 1971. Pestic. Mont. J. 6: 94-96.

Gallagher, J. L. 1974. Sampling macro-organic matter profiles in salt marsh plant root zones. Soil Sci. Soc. Proc. 38: 154-155.

Gallagher, J. L. & Daiber, F. C. 1974. Primary production of edaphic algal communities in a Delaware salt marsh. Limnol. Oceanogr. 19: 390-395.

La Fleur, K. S., Wojeck, G. A. & McCaskill, W. R. 1973. Movement of toxaphene and fluometuron through Dunbar soil to underlying ground water. J. of Environ. Quality. 2: 515-518.

Reimold, R. J. Unpub. ms. Toxaphene interactions in estuarine ecosystems.

Reimold, R. J. & Durant, C. J. 1974. Toxaphene content of estuarine fauna and flora before, during and after dredging toxaphene contaminated sediments. Pestic. Mont. J. 8: 44-49.

Swoboda, A. R., Thomas, G. W., Cady, F. B., Baird, R. W. & Knisel, W. G. 1971. Distribution of DDE and toxaphene in Houston black clay on three watersheds. Environ. Sci. Tech. 5: 141-145.

Taschenberg, E. F., Mack, G. L. & Gambrell, F. L. 1961. DDT and copper residues in a vineyard soil. J. Agric. Food Chem. 9: 207-209.